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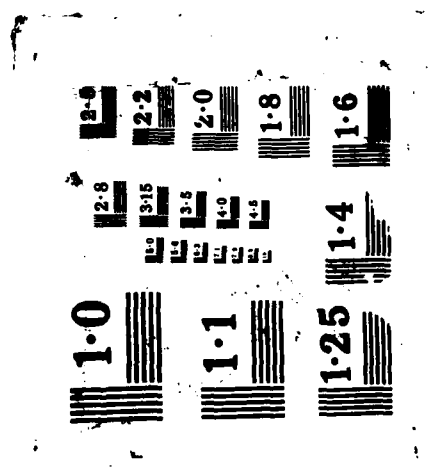
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Applications of Multivalent Ionic Conductors
To Polymeric Electrolyte Batteries

by

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APPLICATIONS OF MULTIVALENT IONIC CONDUCTORS
TO POLYMERIC ELECTROLYTE BATTERIES

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Abstract

The feasibility of solid state cells based upon lithium ion conducting polymer electrolytes has been demonstrated. In the present paper a preliminary investigation of sodium and magnesium ion conductors in polymer electrolyte cells is summarized. Cell types were $\text{Li/V}_6\text{O}_{13}$, $\text{Na/V}_6\text{O}_{13}$, and $\text{Mg/V}_6\text{O}_{13}$ with polymer electrolytes based on polyethylene oxide and salts of the anode element.

1. INTRODUCTION

Polymer electrolytes have been widely investigated over the last ten years because of their potential use in high energy density solid state batteries. Polyethylene oxide (PEO) has been the most extensively studied polymer. It was found that PEO doped with a lithium salt such as LiCF_3SO_3 could give conductivity values of about $10^{-4}(\Omega\text{cm})^{-1}$ at 100°C [1]. Cells utilizing the monovalent salt-polymer electrolyte, lithium anodes and cathodes based on insertion compounds such as V_6O_{13} have demonstrated good cycling and good reversibility at 100°C .

These encouraging results have led to the investigations of other alkali ion systems such as those based on sodium ion conduction. For example, West et al., [2], reported a Na/MoS_3 cell using $(\text{PEO})_{10}\cdot\text{NaI}$ as the electrolyte at 90°C . Worrell et al. reported on a cell Na/TiS_2 , that was operated with $\text{PEO}_{4.5}\cdot\text{NaSCN}$ electrolyte at 80°C [3].

Although exploratory research has also been made on divalent salt systems such as Mg^{2+} , Ca^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} [4-8], little attention has been given to these electrolytes in the studies of solid state batteries. The only report to date has been made by Patrick et al. [8] on a primary Mg/TiS_2 cell using $(\text{PEO})_{15}\cdot\text{Mg}(\text{SCN})_2$ as the electrolyte at room temperature.

The present paper describes the possibility of using V_6O_{13} as the cathode in sodium and magnesium cells and compares the results (where possible) to the performance of lithium cells. The major limitations associated with these cells are also discussed.

2. EXPERIMENTAL

Lithium, sodium and magnesium were chosen as the anode material and V_8O_{13} as the cathode. The technique for preparing the lithium based polymer electrolyte $(PEO)_8 \cdot LiCF_3SO_3$ has been described elsewhere [9]. The sodium ion conductors, $(PEO)_{10} \cdot NaI$, $(PEO)_{10} \cdot NaBr$ and $(PEO)_{10} \cdot NaCF_3SO_3$ and the magnesium ion conductors, $(PEO)_8 \cdot MgCl_2$ and $(PEO)_8 \cdot Mg(ClO_4)_2$ were prepared as follows.

Polyethylene oxide (Polyscience, $MW=5 \times 10^6$), was dissolved in the appropriate amount of acetonitrile. The salts, NaI , $NaBr$, $NaCF_3SO_3$, $MgCl_2$ and $Mg(ClO_4)_2$ were dissolved in the appropriate amount of anhydrous ethanol separately. Each salt solution was mixed with a PEO solution with constant stirring. Once homogenized, the mixture was cast on a PTFE sheet using a doctor blade technique. Using this method, thin films of 15 to 35 μm polymer electrolytes were obtained.

The cathode was prepared by a complex mixing process involving V_8O_{13} (80 w/o), PEO (15 w/o) and Shawinigan carbon black (5 w/o).

A thin, flat sodium electrode was made by placing a piece of sodium on a thin stainless steel surface, covering this with polymer film and compressing the electrode between two glass-slides. Once thin enough, the polymer film was removed from the sodium remaining on the stainless steel current collector. Finally a scalpel blade was used to remove excess sodium and to ensure a smooth, oxide-free surface. The thickness of the sodium film prepared by this means was about 30 μm .

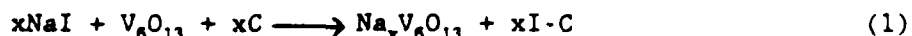
The lithium electrode was obtained as a thin foil (thickness 55 μm) and used with no further treatment. The magnesium electrode was also

obtained as a thin foil (thickness 125 μ m) and after cleaning the surface, the final thickness was about 25 μ m.

Cells were assembled as shown in Figure 1. The diameter of the electrolyte was 1 cm. Adhesive tape (thickness = 50 μ m) was used as the spacer to separate the two electrodes. All the electrolytes were vacuum-dried after casting and stored in an argon atmosphere glove-box for two weeks prior to use. The cell assembly was also carried out in the glove box. Once sealed with epoxy, the cells were tested outside the glove box. Sodium cells were tested at 90°C and lithium and magnesium cells at 100°C.

3. RESULTS AND DISCUSSIONS

The initial open circuit voltages (OCV) of the experimental cells are listed in Table 1. The cells, Na|(PEO)₁₀·NaBr|V₆O₁₃ and Na|(PEO)₁₀·NaCF₃SO₃|V₆O₁₃ show an OCV of about 3.1 V at 90°C. In contrast the Na|(PEO)₁₀·NaI|V₆O₁₃ cell has an OCV of only 2.76V at 90°C. This value is close to the Na|I₂ cell which has an OCV of 2.8 V or 2.9 V, obtained from the free energy of formation of NaI(l) or NaI(s)[10]. This suggests the possibility of a reaction between the NaI and the V₆O₁₃. Two possible reaction schemes are:



Reaction (1) occurs with the adsorption of iodine on the carbon surface and (2) occurs with the liberation of free iodine. In any case both reactions would contribute to a lowering of the OCV.

Both magnesium cells demonstrated an OCV of 2.0 V at 100°C whereas the lithium cell value was greater than 3.2V. The lithium cell was

the most extensively studied system in our investigation. Figure 2 shows the performance of $\text{Li} | (\text{PEO})_8 \cdot \text{LiCF}_3\text{SO}_3 | \text{V}_6\text{O}_{13}$ at three discharge rates. The charging was carried out at constant potential using a limiting resistor in series with the circuit to control the current. At the C/5 rate over a hundred cycles was obtained with greater than 35% of the theoretical capacity ($8\text{Li}/\text{V}_6\text{O}_{13}$). Figure 3 shows the load voltage of the cell against utilization of V_6O_{13} . It is seen that greater than 80% of the theoretical capacity is possible at the C/10 and C/20 rates.

Figure 2 also shows a $\text{Na} | (\text{PEO})_{10} \cdot \text{NaI} | \text{V}_6\text{O}_{13}$ cell operating at the C/4 rate. The cell appears to cycle with constant capacity but is limited to only one Na per V_6O_{13} between the voltage limits of 2.8 V and 1.5 V. A typical charge-discharge curve for the $\text{Na} | (\text{PEO})_{10} \cdot \text{NaI} | \text{V}_6\text{O}_{13}$ cell is shown in Figure 4. The initial stages of discharge appears to be flatter than the latter stages which shows a rapid decline in capacity. The first part is attributed to the reaction of I_2 as shown in sequences (1) and (2) above and the second part to a combination of sodium intercalation with V_6O_{13} and I_2 reaction. During charge the cell potential exceeds 2.8 V when a $51 \mu\text{A}/\text{cm}^2$ charge current is applied. This sudden increase suggests that the intercalation of Na into V_6O_{13} may not be as reversible as Li.

Cyclic voltammetry results on the sodium cells are shown in Figure 5a and 5b. For $\text{Na} | (\text{PEO})_{10} \cdot \text{NaI} | \text{V}_6\text{O}_{13}$, the curve (Figure 5a) shows a distinct inflection at 2.8 V. This is normally representative of a reaction involving



rather than an intercalation reaction ($x\text{Na} + \text{V}_6\text{O}_{13} \longrightarrow \text{Na}_x\text{V}_6\text{O}_{13}$). A typical intercalation curve was found in the $\text{Na} | (\text{PEO})_{10} \cdot \text{NaCF}_3\text{SO}_3 | \text{V}_6\text{O}_{13}$

cell (Figure 5b). This does not show a distinct inflection corresponding to a single reaction but rather a series of reactions.

Due to the low ionic conductivity of the $(\text{PEO})_{10} \cdot \text{NaBr}$ electrolyte, the corresponding cyclic voltammetry curve for the $\text{Na} | (\text{PEO})_{10} \cdot \text{NaBr} | \text{V}_6\text{O}_{13}$ cell exhibited much lower currents (by a factor of 0.001). The curve was representative of a high resistance cell associated with a large iR drop. In contrast the currents were about four times higher in the $\text{Na} | (\text{PEO})_{10} \cdot \text{NaI} | \text{V}_6\text{O}_{13}$ cell than in the $\text{Na} | (\text{PEO})_{10} \cdot \text{NaCF}_3\text{SO}_3 | \text{V}_6\text{O}_{13}$ cell. Furthermore the latter cell demonstrated an order of magnitude increase in the cell internal resistance upon storage for one day at 90°C . This increase in resistance with time was not observed in the other sodium cells. Previous work [11] on the lithium system has demonstrated that LiCF_3SO_3 is not thermodynamically stable with lithium metal. The metal is, however, protected by a passive film formed by a reaction involving the lithium and LiCF_3SO_3 . It is envisaged that NaCF_3SO_3 is also not thermodynamically stable with sodium metal. However, in this case, the protective film appears to be less protective and less ionically conducting than the film on lithium metal. This gives rise to a large build-up of the passive layer which subsequently results in an increase in the interfacial resistance and hence an increase in the observed cell impedance with time.

The cyclic voltammetry curves for the magnesium electrode against a magnesium reference electrode in cells of the type $\text{Mg} | (\text{PEO})_8 \cdot \text{MgCl}_2 | \text{V}_6\text{O}_{13}$ and $\text{Mg} | (\text{PEO})_8 \cdot \text{Mg}(\text{ClO}_4)_2 | \text{V}_6\text{O}_{13}$ are shown in Figure 6a and 6b. In either case the anodic currents are considerably higher than the corresponding cathodic currents. Furthermore the anodic current in the forward potential sweep is less than the anodic current in the backward sweep. In

the forward sweep, the potential of the magnesium electrode increases with a corresponding increase in the slope of the curve. This phenomena does not occur in the backward potential sweep. This clearly suggests the formation of a passive layer on the magnesium electrode surface and, hence, the need to activate the magnesium electrode at a certain potential. However, as the passive film grows with time, the required activation potential increases.

This passivation phenomena can also be confirmed from the voltage delay observed in the constant current discharge curves of the magnesium cells (Figure 7a and 7b). The constant current charge curve shows a poor rechargeability of the magnesium electrodes in both cells.

The cyclic voltammetry curve (Fig. 8) for the V_6O_{13} electrode against a magnesium reference electrode in cells of the type $Mg|(PEO)_8 \cdot Mg(ClO_4)_2|V_6O_{13}$ does suggest some reversibility of magnesium intercalation in V_6O_{13} . The current output in this case is larger than that observed for the magnesium working electrodes.

CONCLUSION

The lithium polymer electrolyte battery system is thus far the best candidate that exhibits good cycling and good reversibility with cathodes such as V_6O_{13} .

Preliminary investigation suggests that the cell $Na|(PEO)_{10} \cdot NaI|V_6O_{13}$ behaves as a $Na|I_2$ cell with an OCV of 2.8V rather than as a $Na|V_6O_{13}$ cell which would have an OCV of 3.1V at 90°C. In addition, passivation in the $Na|(PEO)_{10} \cdot NaCF_3SO_3|V_6O_{13}$ cell and low ionic conductivity of the $(PEO)_{10} \cdot NaBr$ electrolyte severely limits the performance of this system.

The magnesium system is limited by the magnesium electrode rather than the cathode. Further work is continuing to confirm some of the

above observations and to investigate other electrode couples for solid-state polymer-electrolyte batteries.

ACKNOWLEDGEMENT

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TABLE 1. INITIAL OCV OF POLYMER ELECTROLYTE CELLS

	OCV (v)	T(C°)
Li/PEO ₈ LiCF ₃ SO ₃ /V ₆ O ₁₃	3.2	100
Na/PEO ₁₀ •NaI/V ₆ O ₁₃	2.76	90
Na/PEO ₁₀ •NaBr/V ₆ O ₁₃	3.09	90
Na/PEO ₁₀ •NaCF ₃ SO ₃ /V ₆ O ₁₃	3.12	90
Mg/PEO ₈ •Mg(ClO ₄) ₂ /V ₆ O ₁₃	2.0	100
Mg/PEO ₈ •MgCl ₂ /V ₆ O ₁₃	2.0	100

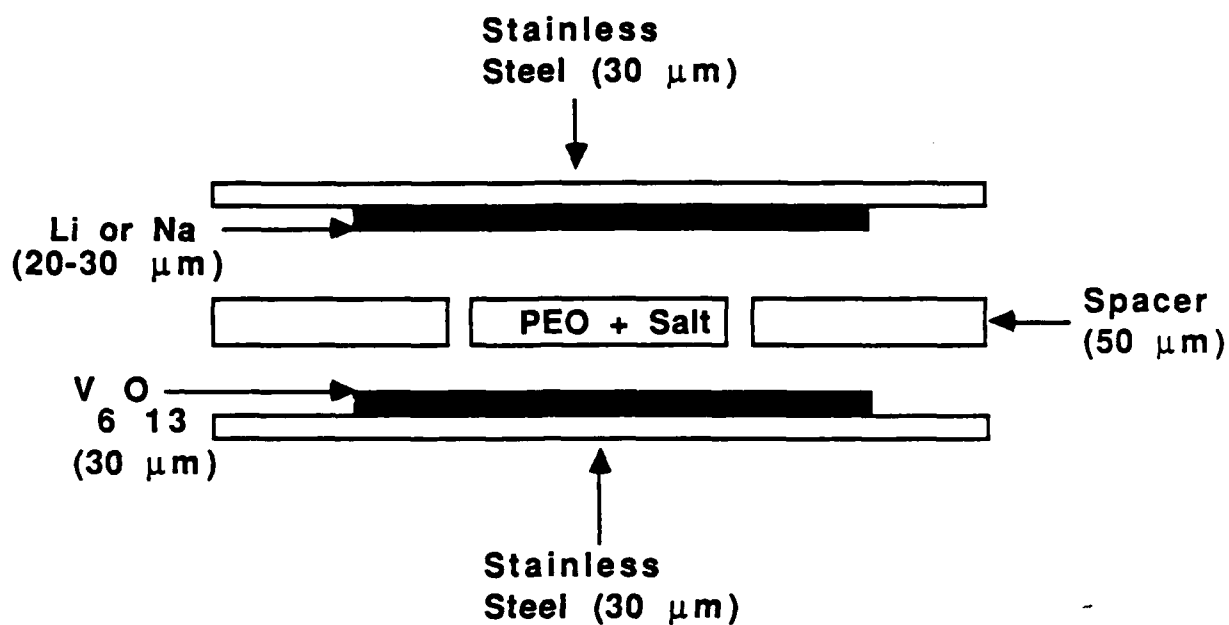


Figure 1. Schematic of a polymer electrolyte cell.

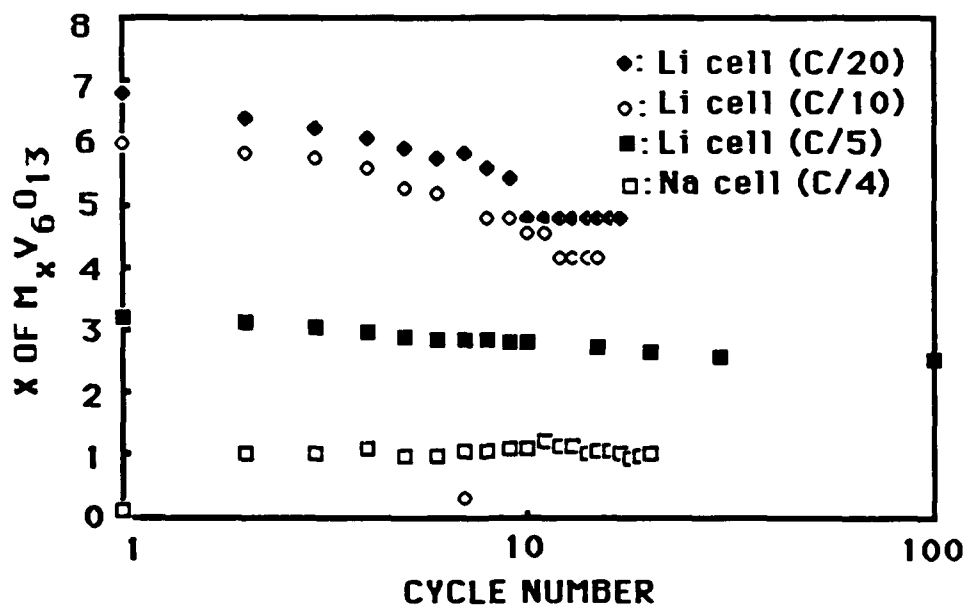


Figure 2. Performance of polymer electrolyte cells.

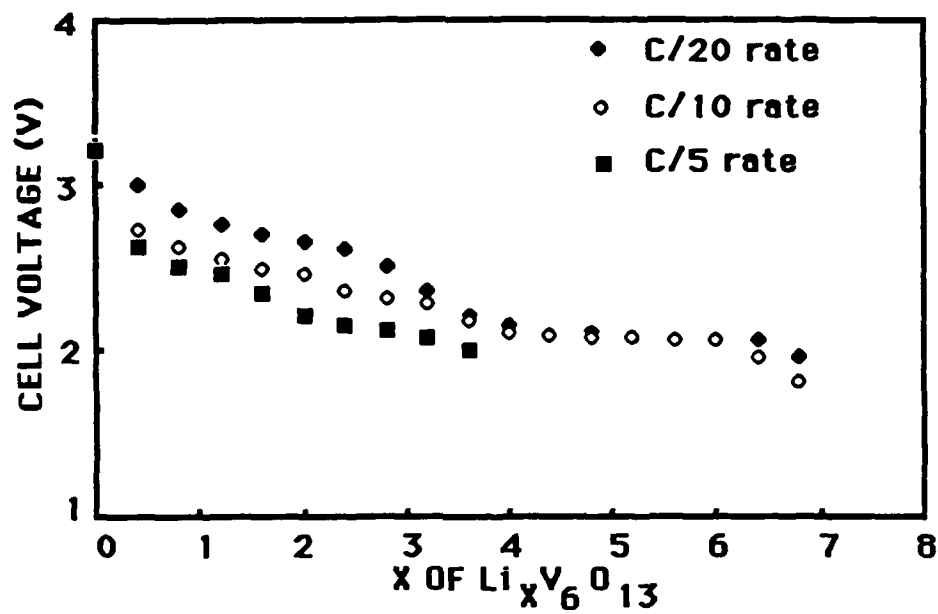


Figure 3. Discharge curve of a $\text{Li}/\text{V}_6\text{O}_{13}$ cell.

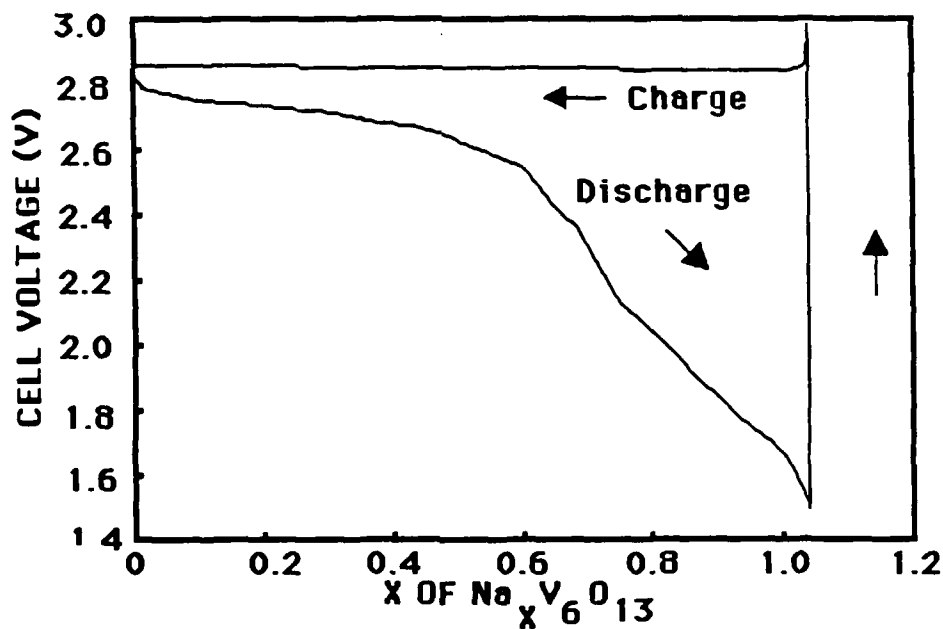


Figure 4. Discharge-charge curve of a $\text{Na}/\text{PEO}_{10}\text{-NaI}/\text{V}_6\text{O}_{13}$ cell at a constant current ($51\mu\text{A}/\text{cm}^2$).

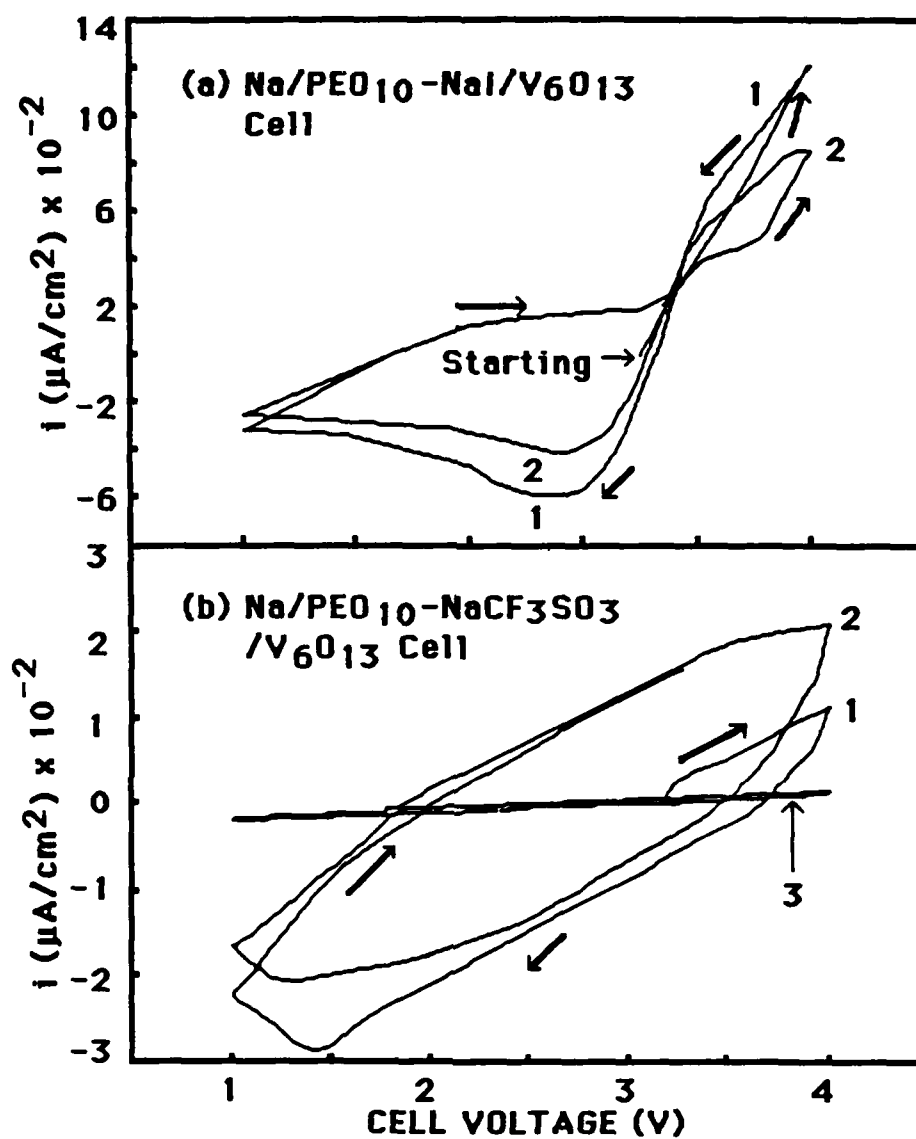


Figure 5. Cyclic voltammograms of sodium cells at 10 mV/s (Cycle 3, after 26 hours storage at 90 °C).

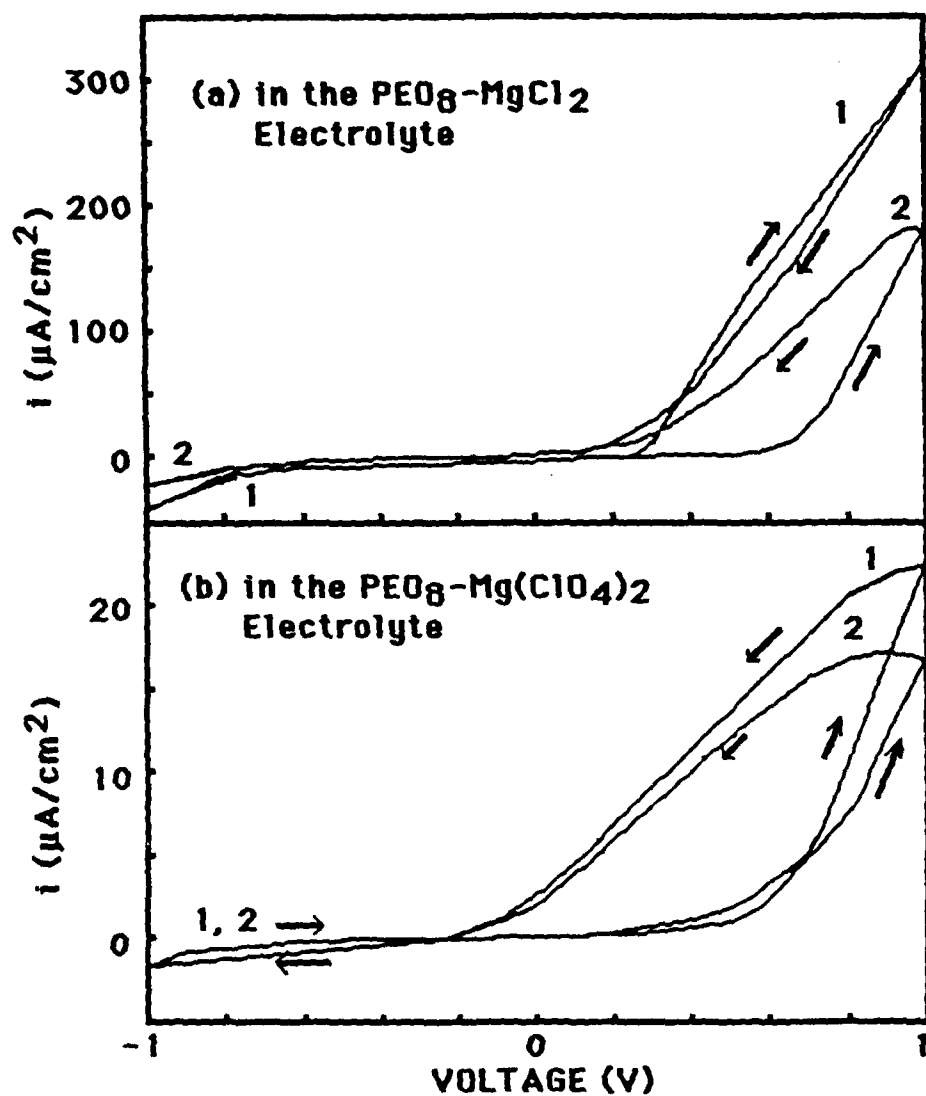


Figure 6. Cyclic voltammograms at 10 mV/s of magnesium electrodes with respect to magnesium ref. electrodes.

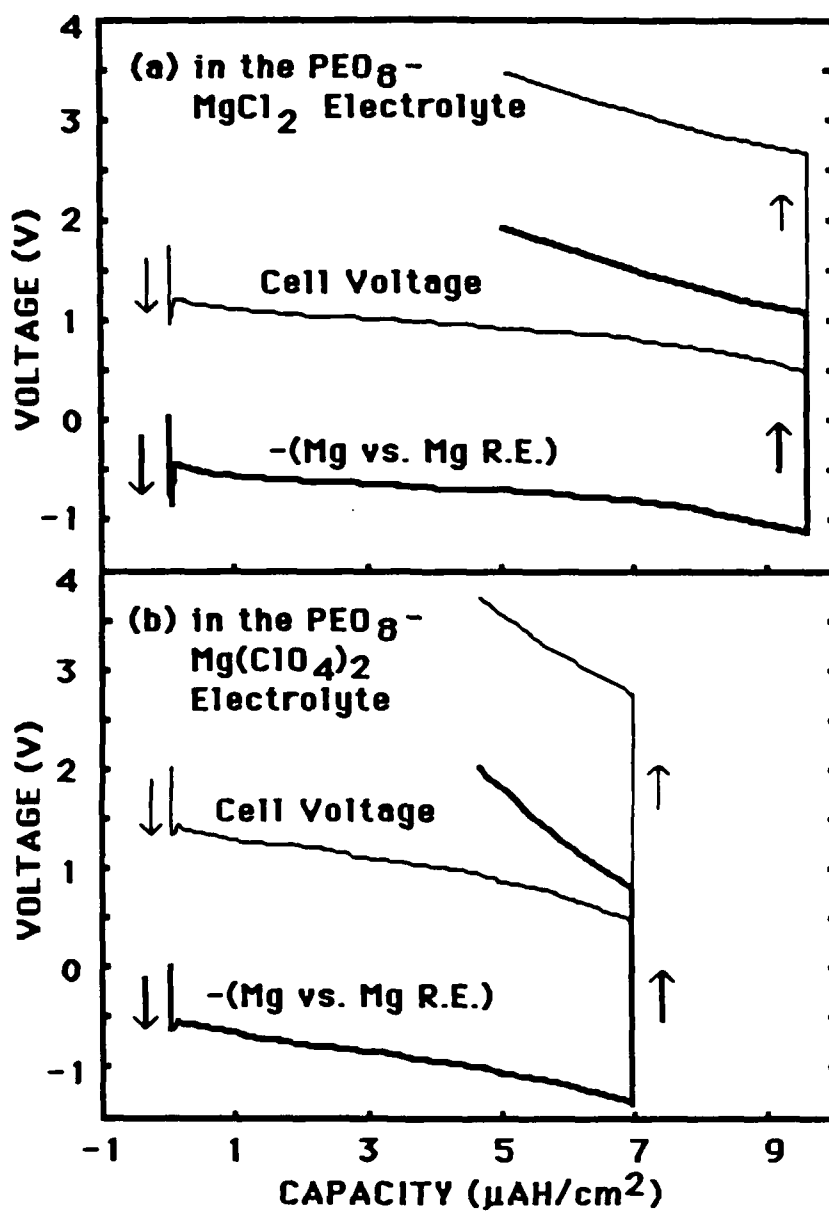


Figure 7. Discharge-charge curves of magnesium cells at a constant current ($16.7 \mu\text{A}/\text{cm}^2$).

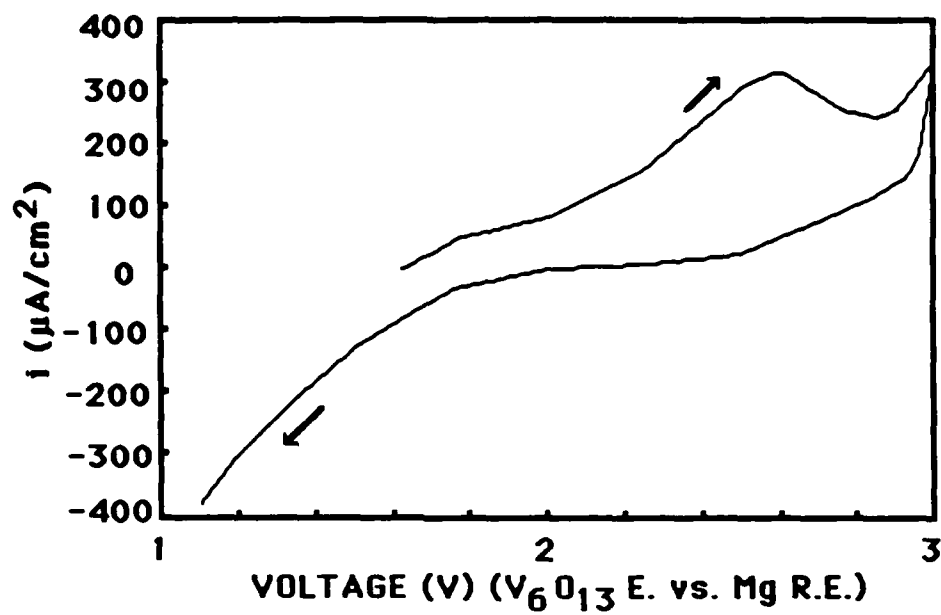


Figure 8. Cyclic voltammogram at 10 mV/s of the V_6O_{13} electrode in the $\text{PEO}_8\text{-Mg}(\text{ClO}_4)_2$ electrolyte.

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